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Quantification of the maleic anhydride grafted onto polypropylene by chemical and viscosimetric titrations, and FTIR spectroscopy

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Abstract

An acid–base titration method for an accurate and reproducible quantification of maleic anhydride grafted onto polyolefins is proposed. The use of an organic base (tetra-butylammonium hydroxide) enhances the base solubility in organic solvents and prevents phenomena like coarcervation. The titration goes on until the visual endpoint of a coloured indicator, corresponding to the neutralisation of the grafted functions. Bromothymol blue is chosen as the coloured indicator to determine this equivalence point.

It is critically correlated with a Fourier transform-infrared spectroscopy quantification developed previously by De Roovers et al. [J Polym Sci, Part A: Polym Chem 1995;33:829] and with a viscosimetric titration method here-proposed. Finally, the titration mechanism is confirmed by the titration of some well-defined amount of anhydride model compounds and by FTIR analyses of their products after titration. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Maleic anhydride grafted polypropylene; Quantification; Titration

1. Introduction

In recent years, many quantitative analyses of particular reactive functional groups present on high polymers have been developed. For this purpose, Fourier transform-infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), gas chromatography (GC) and titration techniques were mostly used.

In this context, the present article aims to quantify the anhydride content grafted onto polyolefins by titration.

In order to quantify the concentration of anhydride groups bound onto polyolefins, an acid–base titration is often chosen [1–14], but potentiometric and conductimetric acid–base titrations are also used [15–17]. All except one of them have resulted, probably, from a rapid transposition of the acid–base titration techniques developed for aprotic or inert solvent at room temperature [18–22], to the more complicated case of polyolefins. Hence, they came up against problems. The study issued by Ganzeveld and Janssen [11], used a more adapted-titration method, but it needed an additional refinement. Therefore, we describe here, step by step, the selection of our proposed method, in view of showing where the traps are and how they may be avoided.

We claim that this method is more reproducible and accurate than the previously proposed ones. Indeed, by the use of model compounds of anhydride functionalised polyolefins, the chemical reactions occurring during the titration are clearly assigned, and hence the stoichiometry of the titration. Moreover, the titration of a well-defined amount of those model compounds confirmed the accuracy of the method.

Finally, the results obtained for a few samples of PP-g-MA—thanks to the titrimetric method, are confronted to those obtained in the FTIR spectroscopy quantification and to a recently developed viscosimetric titration.

1.1. Background

Acid–base titrations of maleic anhydride grafted polyolefins are commonly performed in aromatic solvents such as xylene or toluene. Other studies also mention the use of a butanol–xylene mixture [11], or even a titration method on a polyethylene suspension in xylene [2].

The solvent used is pure or saturated with water leading to quantification of the anhydride groups or their hydrolysed form, respectively.

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Work in dry conditions requires a previous vacuum–thermal treatment of the polyolefins to ensure the total conversion of the grafted maleic anhydride in its anhydride form. The results of 1–3 days at 75–120°C are generally reported [3,4,8,16].

Conversely, in wet organic solvents, all the cyclic anhydride functions have to be opened into carboxylic acid groups. The solvent is saturated with water [5–7,9], or added with 200 μl of water after matrix dissolution [1,10]. The hydrolysis is carried out by refluxing in solvent for 1–1.5 h [1,5,10].

Finally, when alcohol in non-aqueous solvents is used, it opens the anhydride ring, into an ester function and an acid function [4–17].

The titration goes on until the visual endpoint of a coloured indicator, corresponding to the neutralisation of the grafted functions. Thymol blue is often chosen as the coloured indicator to determine this equivalence point [3–9,11].

In some cases, phenolphthalein in an alcoholic solution is used [1,2,9,15].

The titration agent is an alcoholic base solution, most often KOH in ethanolic solution [1,3,4,8,10,12]. Only once, a solution of tetra-butyl ammonium hydroxide (TBAOH) free of water is noted [11].

Other authors use a back-titration method adding an excess of base to the solution and titrating it back with HCl [2,5–7,9,13].

Although some studies (among which, one was performed in our laboratory [1]), attempted to confirm the results of the presented methods—thanks to correlations with FTIR measurements [1,4]; more recent results obtained by our team point out a lack of reproducibility in the titration methods [10].

2. Experimental

2.1. Materials

Toluene, methanol, ethanol (Merck-Belgolabo, AR grade), succinic anhydride (Aldrich, 99% purity), *m*-xylylene diamine (Janssen Chimica, 99% purity), *n*-octadecylsuccinic and 2-dodecenylsuccinic anhydride (Alfa Product, 99% purity), KOH (Acros Organics, AR grade) were used without further purification.

TBAOH (0.1N) in toluene–methanol, tetra-methyl ammonium hydroxide 20% in methanol solution and HCl (0.1N) in isopropanol were purchased, respectively, from Acros Organic, Aldrich and Merk-Belgolabo.

Phenolphthalein, thymol blue and bromothymol blue came from Sigma.

Pure polypropylene (PP Eltex HF001P 25976) and the organic peroxide (DHBP-Interox, Peroxid Chemie) were kindly supplied by Solvay Company. Solvay also provided polypropylenes with increasing MA graftings, noted as PP-g-MA002, PP-g-MA003 and PP-g-MA004. To test more PP-g-MA, other samples were synthesised in our laboratory or chosen amongst commercial polypropylenes with known AM contents [10].

2.2. Grafted polyolefins synthesis

The grafted polyolefins were synthesised in a Brabender Plasticorder equipped with an electrically heated W50EH mixing device of about 50 ml volume. The oxidation of the mixed polymers was largely reduced by a nitrogen flow of 5 l/min above the mixing chamber. No mechanical pressure was applied onto the polymer during mixing. The polymer weight processed in the Brabender plastograph was 40 g. All the reactants (maleic anhydride, DHBP-Interox peroxide and polyolefins) were dry mixed together before their quick introduction (less than 1 min) into the preheated Brabender plastograph. The mixing speed was fixed at 75 rpm for 4 min, and the temperature at 200°C.

2.3. Analytical characterisation of anhydride content

Before titration, grafted polyolefins were treated in a vacuum oven for 24 h at 110°C in order to sublimate the unreacted maleic anhydride. This treatment also performs the complete cyclisation of the carboxylic acids into a carboxylic anhydride form.

2.3.1. Acid–base titrations

A few milligrams of model compounds or 1 g of grafted polyolefins were dissolved in 150 ml of toluene at boiling temperature. Polyolefins were always fully soluble and did not precipitate during the titration.

The TBAOH was added, just after the coloured indicator (five drops of 1% (w/v) bromothymol blue in methanol), by a conventional 10 ml microburet (0.02 ml divisions) or by an automicroburet, controlled by a 655 dosimat line-operated pH meter from Metrohm at a rate of 0.1 ml/min. The titration was stopped at the visual endpoint when the colour change was stable. The AM content was then calculated from the titrating agent's volume and its concentration.

For the acid–base potentiometric titrations, the pH meter was equipped with a S508B combined glass–membrane electrode and a standard calomel electrode, provided with a free-flow sleeve junction coming from Consort N.V.

2.3.2. Viscosimetric titrations

Viscosimetric titrations were also carried out in the Brabender.

A mechanical pressure was applied onto the polymer for the whole mixing. The mixing speed was fixed at 75 rpm and the temperature was held at 190°C.

One minute after the torque stabilisation, a known volume of *m*-xylylene diamine was introduced in the mixing chamber, under continuous mixing with a glass microsyringe.

The reaction was stopped immediately after the torque-top.

Different mixings were recorded with increasing amounts of *m*-xylylene diamine. The resulting torque-top diagram allows us to quantify the anhydride concentration on polypropylene as further detailed.

2.3.3. Size exclusion chromatography

Molecular weight measurements of PP-g-MA mixed with *m*-xylylene diamine, were carried out by high temperature, size exclusion chromatography (SEC). The chromatograph was a Waters 150C equipped with 2 Shodex columns—AT-80M/S, and 1 Shodex column—Styragel 300 Å. A differential refractometer–detector coupled with a "microVax Data Station" provided by Digital was used for recording and analysing the signal. The permeation solvent was vacuum distilled 1,2,4-trichlorobenzene, stabilised with 2% Irganox 1010. The sample's dissolution was achieved at 160°C for 1 h. The concentrations ranged from 6 to 8 mg/ml. The injection volume was 120 μl. The system was maintained at 135°C for the analyses.

A polypropylene calibration was used for the SEC analyses.

2.3.4. FTIR spectroscopy

2.3.4.1. Anhydride quantification The FTIR spectra were recorded on a Perkin–Elmer FTIR Spectrometer 1760-X from 4000 to 400 cm^{-1} with a 0.5 cm^{-1} resolution.

The polyolefins samples were processed in 100 μm films, by compression moulding of a 0.1–0.2 g sample between Teflon-covered aluminium sheets under 1 MPa pressure at 190°C for 5 s. Before quantification of the maleic anhydride grafted onto polypropylene, the films were dried at 110°C for 24 h under vacuum.

The sublimation and the cyclisation of unreacted maleic anhydride were ascertained by FTIR controls, respectively, by the disappearance of the characteristic absorption band at 720 cm^{-1} associated with the CH out-of-plane deformation of maleic anhydride, and by the disappearance of the absorption band at 1715 cm^{-1}, assigned to the carboxylic acid.

The quantification of the maleic anhydride grafted onto polypropylene was performed following a previously reported method [1]. The calibrations were realised for the *n*-octadecylsuccinic anhydride and the polymaleic anhydride dispersed in polypropylene in a concentration range from 10 to 40 μeq/g of anhydride functions mixed in 1 g of polymer. The IR spectra of the mixtures were mathematically analysed by an iterative curve-fitting method developed in the software "Igor" provided by Wavemetrics, Inc. The absorption bands in the carbonyl frequency range of the anhydride (1650–1850 cm^{-1}), and in a region characteristic of the polymer (1050–1150 cm^{-1}) used as reference, were approximated by Lorentzian functions [23].

The amplitudes of the so-obtained Lorentzians (considered as the actual absorption bands), are used for the calibration leading to the following calibration curve equations:

$$[\text{succinic anhydride}] = 21.5\ (\text{abs } 1792\ \mathrm{cm}^{-1}/\text{abs } 1100\ \mathrm{cm}^{-1})$$

$$[\text{polyanh. anhydride}] = 51.3\ (\text{abs } 1784\ \mathrm{cm}^{-1}/\text{abs } 1100\ \mathrm{cm}^{-1})$$

where:

- [anhydride] is the anhydride concentration expressed in μeq/g;
- abs 1792 cm^{-1} is the absorbance of succinic anhydride symmetric C=O stretch;
- abs 1784 cm^{-1} is the absorbance of polymaleic anhydride symmetric C=O stretch;
- abs 1100 cm^{-1} is the reference absorbance for classic isotactic polypropylenes.

The absorbance value was taken as the maximum value of the Lorentzian curves obtained by curve fitting.

2.3.4.2. Hydrolysis and its analysis The efficiency of the hydrolysis of the anhydride functions was controlled by FTIR on the PP-g-MA 002 after its treatment in conditions similar to the ones used in the proposed acid–base titration method. After dissolution of the polymer in toluene at boiling temperature, 50 μl of water with and without the same volume of pyridine or dimethhylformamide (DMF), were added. The reflux temperature was maintained for 2 h before the sample precipitation into acetone. The samples were repeatedly washed with acetone and dried under vacuum at room temperature for 24 h.

2.3.4.3. Chemical reactions during titration and their analyses The FTIR spectra of the polymer just after the coloured indicator addition and at the neutralisation completion of the anhydride functions were studied in the same way as described above.

2.3.4.4. Thermal oxidation observation Films of polypropylene mixed into the Brabender plastograph with and without 0.25% of DHBP-Interox peroxide, were dried at 110°C for, respectively, 24, 48 and 72 h, in view of observing by FTIR an eventual thermal oxidation.

3. Results and discussion

3.1. Advice against drawbacks in acid–base titrations of maleic anhydride grafted polyolefins

In a previous work [10], we pointed out the low reproducibility of the titration method used in our first publication on grafted PP [1]. A variation of about 40% between measurements was noticed.

A direct transposition of the classic acid–base titrations to the polymer titration led to many drawbacks.

The first drawback originates in the lack of mineral base

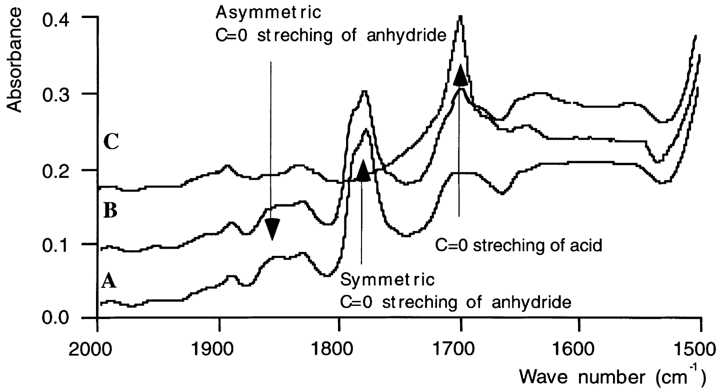

Fig. 1. Hydrolysis check of the anhydride grafted onto polypropylene. Infrared spectra recorded between 2000 and 1500 cm^{-1} on a PP-g-MA002, previously dried at 110°C for 24 h. (A) without hydrolysis attempt, (B) after a reflux for 2 h in Toluene-H_2O ($1/3 \times 10^{-3}$ (v/v)), (C) after a reflux for 2 h in Toluene-H_2O-Pyridine ($1/3 \times 10^{-3}/3 \times 10^{-3}$ (v/v/v)).

solubility into aprotic solvents. KOH (or HCl in the case of a back-titration), i.e. a mineral base (or a mineral acid) has to be first dissolved into an alcoholic solvent miscible into xylene or toluene. In addition, the neutralisation of the grafted functions in direct titrations (or in back-titration) has to arise quickly to avoid the base precipitation (or the acid evaporation) because of the hot aprotic environment necessary for polyolefin solubilisation.

Moreover, other parameters can lead to an inhomogeneity of the titration medium. Hence, the volume of alcoholic solvent, which is a bad solvent of the polyolefins but used only to convey the mineral base or acid into the organic solvents, should not be too important; otherwise there would be a risk of polymer precipitation during the titration and hence, of inaccurate results.

Similarly, when the titration method requires water to hydrolyse the anhydride function, the process has to be correctly supervised to prevent the formation of a distinct aqueous phase from the acid neutralisation.

Finally, coacervation phenomena due to inter- and/or intramolecular crosslinkings between nonadjacent carboxylic acid groups are mentioned when a base with a small univalent metallic cation is used for the titration [12,24].

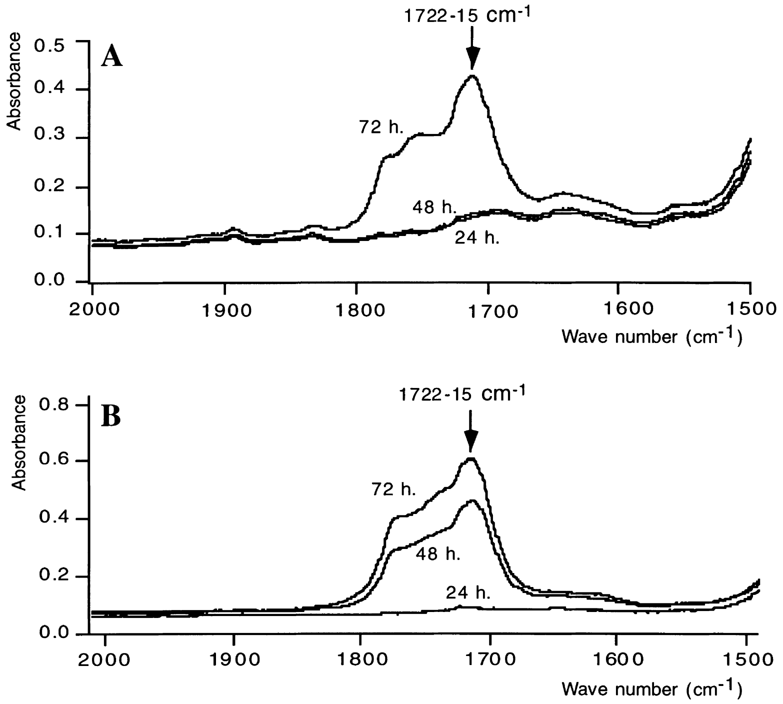

Fig. 2. Observation of a thermal oxidation of the polypropylene by FTIR. Infrared spectra recorded between 2000 and 1500 cm^{-1} on a PP Eltex film before (Spectrum A) and after its processing with 0.25% of DHBP-Interox peroxide (Spectrum B). The spectra are recorded after different drying times (24, 48, 72 h) at 110°C under vacuum.

Another drawback encountered in most reported titrations methods was a stoichiometry heterogeneity of the neutralisation. The presence of a primary alcohol in the titration medium converts the anhydride functions into ester and acid functions, while the geminated acid groups coming from the hydrolysis of anhydride functions are not esterified. This is the case when the coloured indicator dissolved in alcohol is added just before the addition of the base. This is reported to be also the case when the quantification of the anhydride functions proceeds through a base dissolved in an alcoholic solution [2,4,17].

A different reaction stoichiometry between the anhydride form and the corresponding acid distorts the grafted functions quantification when both forms are present [4,22]. Therefore, on the one hand, in many reported methods, a full hydrolysis of the anhydride is proposed before titration; based on a total conversion of the anhydride groups into their corresponding acid. However, in Fig. 1, IR spectra of a PP-g-MA before (Spectrum A) and after a 2 h hydrolysis at reflux temperature in toluene with 50 μl water (Spectrum B) shows very few transformations of the grafted maleic anhydride groups into their acidic forms. The band at 1715–1720 cm^{-1} due to the formation of carboxylic groups starts to emerge. It is compensated by a slight decrease of the carbonyl band at 1785–1790 cm^{-1} characteristic of anhydride functions. A full hydrolysis of anhydride functions is only obtained when a small amount of pyridine is added. The pyridine is known to catalyse the hydrolysis [22,24,25]. The IR spectrum of a PP-g-MA after a 2 h hydrolysis at reflux temperature in toluene added with 50 μl of water and the same volume of pyridine (Fig. 1, Spectrum C) shows a complete anhydride conversion into the acid forms (disappearance of the anhydride groups at 1785–1790 cm^{-1} and appearance of acid functions at 1715–1720 cm^{-1}). A similar improvement of the hydrolysis of anhydride has also been obtained with a DMF addition.

No influence of pyridine on the titrimetric results was noticed.

On the contrary, other methods propose to close all the anhydrides before titration. A preliminary drying of the polymers is applied for this purpose. This, later, not only converts all grafted diacid functions into anhydride, but also eliminates ungrafted maleic anhydride out of the matrix.

It is to be emphasised here that a soft drying has to be applied, because exaggerated times and temperatures, especially when initiation by peroxides [26,27] is possible, give thermo-oxidative degradation and creation of new functions, like carboxylic groups among others. As an example, the IR spectrum of a polypropylene (PP Eltex) melt mixed with the DHBP-Interox peroxide, shows, in Fig. 2, a faster increase of the carbonyl band at 1715–1720 cm^{-1} due to the formation of carboxylic groups than observed onto the crude polymer (9 μeq of carboxylic functions/g of polymer is titrated after 60 h at 100°C under vacuum).

Drying in a vacuum oven at 110°C for 24 h was sufficient to eliminate ungrafted maleic anhydride from the matrix, and to close all grafted succinic acids without significant side formation of oxidative acid groups.

The use of an organic base such as the TBAOH is proposed here, because it avoids most of the previously developed drawbacks. First, the presence of alkyl substituents on the molecule enhances its solubility in organic solvents and allows us to get rid of most of the solubility problems. Moreover, coacervation phenomena should not occur when TBAOH ion is used, since it appears to be too large to fit the available space to give coacervation during titration [23].

The choice of this base leads us to revisit the choice of the coloured indicator.

The acid–base neutralisation in the PP-g-MA acid–base titration is fixed thanks to the visual endpoint obtained by the colour change of an indicator. The choice of the coloured indicator is thus determining for the equivalence point detection. Fig. 3(A) reports the succinic anhydride potentiometric titration curve as well as the colour modification zones of various indicators in our titration conditions. Only the bromothymol blue in our titrimetric conditions presents a clear-cut colour change from yellow to blue at the equivalent point corresponding to the consumption of one mole of TBAOH by a mole of succinic anhydride. Fig. 3(B) exhibits the same clear-cut colour change of bromothymol blue, at the equivalence point for a dry PP-g-MA003, when an acid–base potentiometric titration with TBAOH is carried out.

The choice of the coloured indicator still needs a close control of the neutralisation mechanism in view of determining the stoichiometry grafted anhydride functions towards the TBAOH.

3.2. Study of the mechanism of the reaction occurring during titration

During the methanolic solution addition of the coloured indicator, the anhydride functions can react with the alcohol to form an ester function and an acid function (Fig. 4; Reaction I). The IR spectrum of a PP-g-MA just after the addition of the coloured indicator (Fig. 5) shows a decrease of the carbonyl band at 1785–1790 cm^{-1}, assigned to the anhydride functions. Simultaneously, an apparition of two bands is observed: the first one at 1710 cm^{-1}—assigned to carboxylic acid function, and the second one at 1727 cm^{-1}—assigned to the ester function. A total conversion is not observed. Two species are present: an anhydride form and its corresponding ester–acid form.

Similarly, a methanolate form of the TBAOH (TBAOMe) is assumed possible (Fig. 6; Reaction II) due to its methanolic environment. This does not affect the titration results, because the anhydride functions and the corresponding ester–acid form may react in the same stoichiometry balance towards TBAOH whatever its form.

Therefore, four reactions are thus assumed possible (Figs. 7–10; Reaction III–VI), because no $\mathrm{p}K_\mathrm{a}$ or $\mathrm{p}K_\mathrm{b}$ calculations

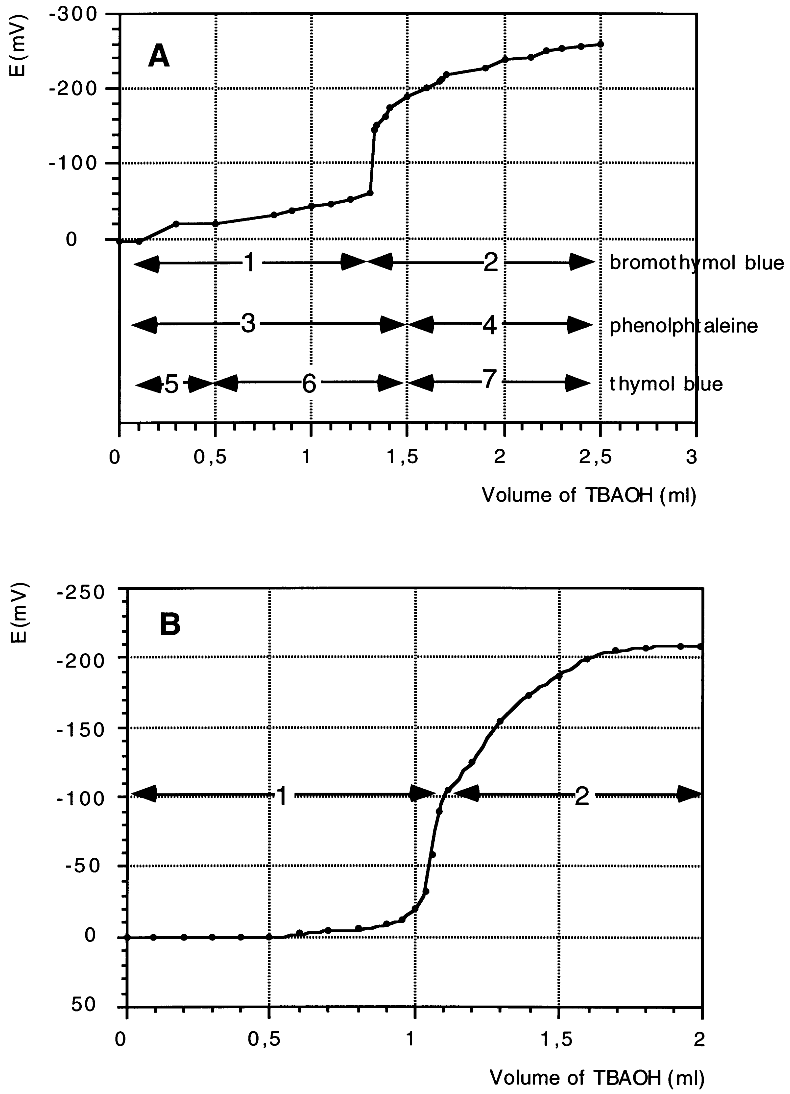

Fig. 3. (A) Potentiometric titration of succinic anhydride and the colour zones for the bromothymol blue (1, yellow; 2, blue), the phenolphtalein (3, colourless; 4, red) and for the thymol blue (5, yellow; 6, orange; 7, blue) and PP-g-MA 003, (B) potentiometric titration of and the colour zones for the bromothymol blue (1, yellow; 2, blue).

help to solve the actual route due to the aprotic or inert solvent.

The acid from the ester–acid forms is neutralised by the TBAOH (Fig. 7; Reaction III) or the TBAOMe (Fig. 8; Reaction IV) to form the salt of the carboxylic acid. It is the classic case of a weak-acid neutralisation by a strong base.

The methanolate, which is a strong base (very nucleophilic) reacts onto an anhydride group to form directly one ester

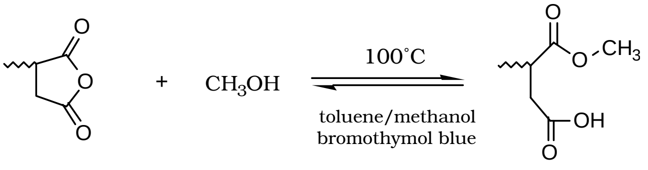

Fig. 4. Reaction I.

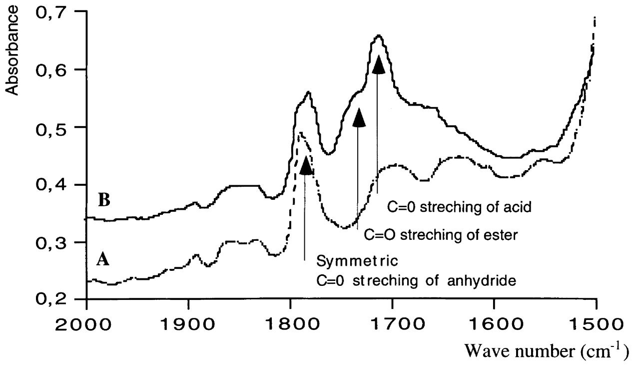

Fig. 5. Infrared spectra between 2000 and 1500 cm^{-1} of PP-g-MA002 before (A) and after (B) the addition of the bromothymol blue methanolic solution.

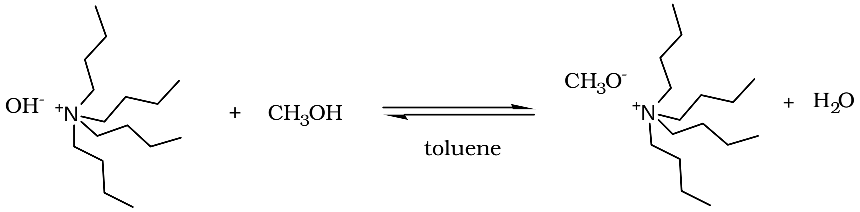

Fig. 6. Reaction II.

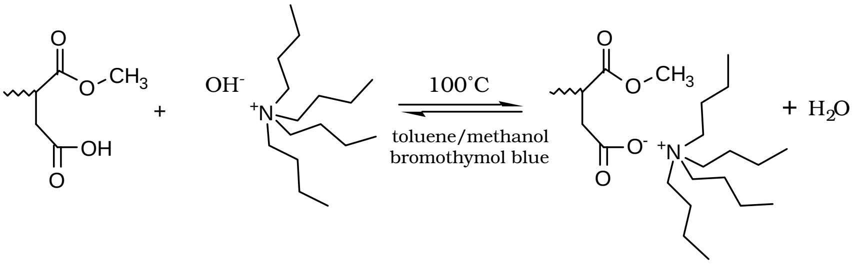

Fig. 7. Reaction III.

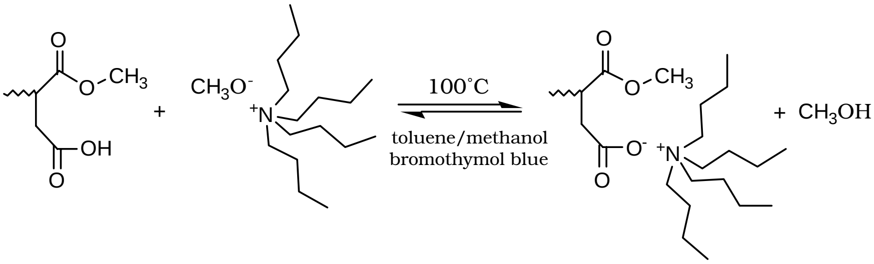

Fig. 8. Reaction IV.

and one salt of the carboxylic acid (Fig. 9; Reaction V). As shown in Fig. 11, the total conversion of the anhydride groups into ester and salt functions occurs at the acid–base neutralisation. A disappearance of the anhydride bands at 1785–1790 and 1850 cm^{-1} (respectively due to symmetric and asymmetric C=O stretching of anhydride functions) is balanced by the appearance of the ester and salt bands (respectively pointed at 1727 and 1590 cm^{-1}). No absorption band at 1715 cm^{-1} assigned to the carboxylic acid is observed: the acid supposed to be formed is either probably esterified by methanol as soon it is formed, or the reaction between the anhydride form and the TBAOH (Fig. 10; Reaction VI) is improbable.

We can conclude that whatever the case, the grafted anhydride stoichiometry with TBAOH is one mole of base for one mole of anhydride.

The model compounds (*n*-octadecylsuccinic anhydride (ODSAnh), 2-dodecenylsuccinic anhydride (DSAnh) and its corresponding acid (DSac) show a one-to-one stoichiometry towards the TBAOH (Table 1), ensuring that as much salt as ester is formed during the titration.

To reach the second acidity when a diacid form on polypropylene is present, not only a suitable coloured indicator is required but also a less-bulky base than TBAOH. An accurate quantification of the two acids of the anhydride functions has been performed by using the tetra-methyl ammonium hydroxide in the presence of thymol blue (Table 1). The esterification of the acid functions by methanol during titration does not occur in these conditions.

Therefore the diacid forms do not disturb the titrimetric stoichiometry, because the colour change of the bromothymol blue is observed, just at the neutralisation of the first acid function (Fig. 12; Reaction VII). The TBAOH consumption is similar for PP-g-MA whether it is closed or open.

The choice of the coloured indicator is thus the main novelty of the proposed-titration method in comparison with the Ganzeveld–Janssen's method. To the best of our knowledge, bromothymol blue has never been proposed as an indicator agent in the PP-g-MA titration, although its colour change is the only one well located. In the Ganzeveld–Janssen method, we observed that the results overestimate the anhydride concentration by about 20%, because of too late equivalence point detection.

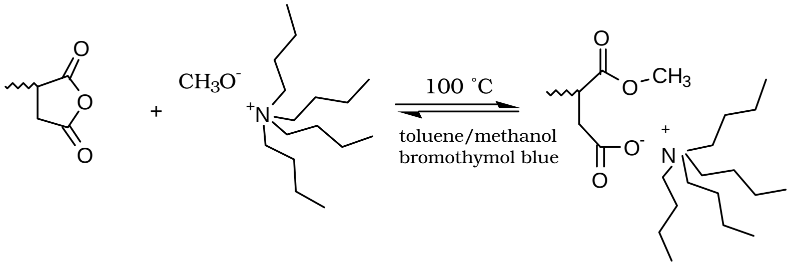

Fig. 9. Reaction V.

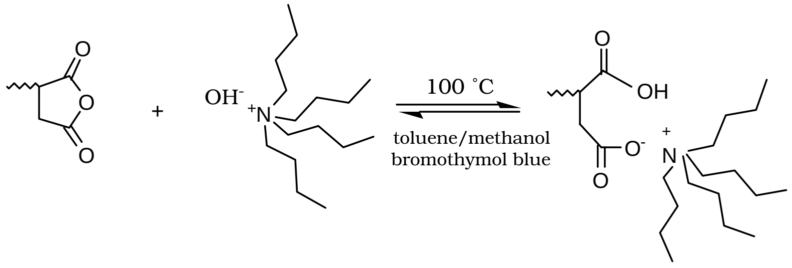

Fig. 10. Reaction VI.

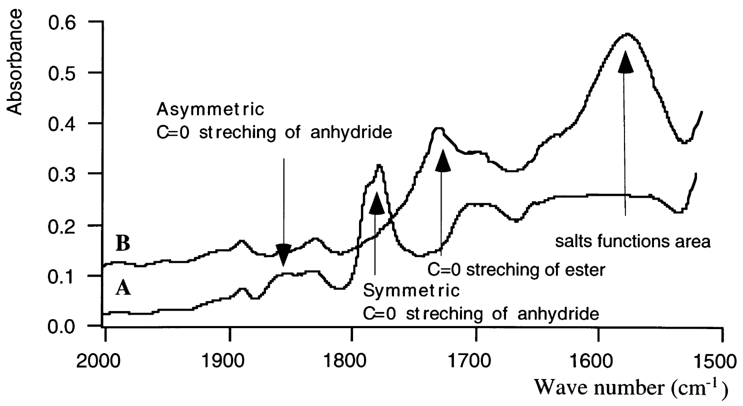

Fig. 11. Infrared spectra recorded between 2000 and 1500 cm^{-1} on PP-g-MA002 before (A) and after the acid–base titration (B).

3.3. Comparison of the acid–base titration with other methods

The anhydride concentrations of the three variously grafted PP-g-MA (PP-g-MA 002, PP-g-MA 003 and PP-g-MA 004) are measured out—thanks to the here-proposed method. The results are presented in Table 2. For each sample, five titrations were performed for estimating the reproducibility of the method.

The total amounts, observed by the here-proposed titration method, grafted onto the PP-g-MA 002, PP-g-MA 003 and PP-g-MA 004 are, respectively, 37.2 ± 0.8, 20.4 ± 1.4 and 11.4 ± 0.5 μeq/g.

After titration completion, an IR spectrum of each product is realised. In each case, a total disappearance of the anhydride bands is observed.

In view of ascertaining the titration method, anhydride concentrations calculated from FTIR and viscosimetric dosages were compared to the titration results.

On the basis of our previously described FTIR method [1], which allows us to quantify different anhydride species grafted onto polypropylene, the three PP-g-MA samples have been analysed. Table 2 gives the amount of each anhydride species calculated (a) by a mathematical iterative-curve fitting of the anhydride absorption bands localised between 1650 and 1850 cm^{-1}, and (b) by the use of a calibration performed on model compounds representative of maleic anhydride grafted onto polypropylene chain-ends following a β-scission mechanism. Our grafted species assignments are succinic anhydride and low molecular mass poly (maleic anhydride) chain-ends. It is to be noted that these grafted species are controversial: other authors

Table 1
Titrimetric stoichiometric's results of different model compounds of anhydride functionalised polyolefins (maleic anhydride, succinic anhydride, *n*-octadecylsuccinic anhydride (ODSAnh), 2-dodecenylsuccinic anhydride (DSAnh) and 2-dodecenylsuccinic acid (DSAc)) in function of the choice of the titrating agent (tetra-butyl ammonium hydroxide (TBAOH), tetra-methyl ammonium hydroxide (TMAOH)) and the coloured indicator (bromothymol blue (BTB), thymol blue (TB))

Model compounds identification	Titrating agent -coloured indicator	Introduced amount (mole)	Titrated amount (mole)	Stoichiometry
Maleic anhydride	TBAOH-BTB	2.30×10^{-4}	2.27×10^{-4}	1
Succinic anhydride	TBAOH-BTB	2.90×10^{-4}	2.80×10^{-4}	1
ODSAnh	TBAOH-BTB	6.50×10^{-5}	6.40×10^{-5}	1
DSAnh	TBAOH-BTB	2.35×10^{-3}	2.34×10^{-3}	1
DSac	TBAOH-BTB	8.40×10^{-4}	8.50×10^{-4}	1
DSac	TMAOH-BTB	8.40×10^{-5}	1.30×10^{-4}	1.5
DSac	TMAOH-TB	8.10×10^{-5}	1.70×10^{-4}	2

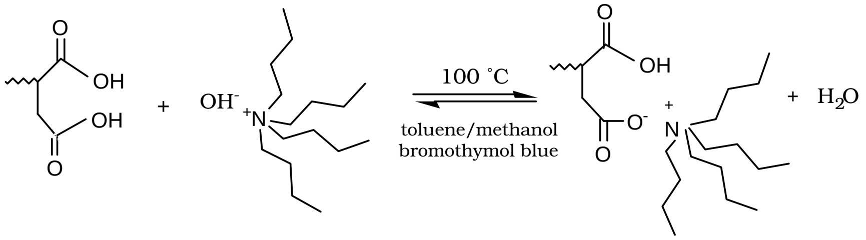

Fig. 12. Reaction VII.

have proposed other grafting mechanisms and other types of anhydrides [28,29].

The results presented originate from the average of five repeated analyses.

The total amounts, detected by the FTIR method, grafting onto the PP-g-MA 002, PP-g-MA 003 and PP-g-MA 004 are, respectively, 43.8 ± 1.9, 22.3 ± 1.1 and 11.0 ± 1.5(μeq/g).

The total concentration of grafted anhydrides was also estimated by a viscosimetric measurement. This method consists in a PP-g-MA melt mixing in the presence of a known *m*-xylylene diamine amount. The diamine reacts with the anhydride functions and provides bonds between PP-chains. For the various diamine ratios, the maximum mixing torque revealing the maximum chain lengthening, is measured. Until the introduced diamine amount does not exceed half the grafted anhydride concentration, the chain lengthening occurs and the torque increases. Just above this critical concentration, the diamine in excess ends the polypropylene without a systematic lengthening production. The torque does not increase so much. The equivalence is thus reached.

In view of minimising and equalising the mixing times for

Table 2
Results of anhydride concentration grafted onto PP-g-MA 002 to 004 measured out by FTIR (average of five measurements), viscosimetric (one measurement) and acid–base titrimetric methods (average of five measurements) (σ: standard deviation)

Sample identification	Anhydride content (μeq/g PP (σ))				
	Acid–base titration ($n = 5$)	FTIR ($n = 5$)			Viscosimetric titration ($n = 1$)
		Grafted succinic anhydride content	Grafted polyanhydride content	Total grafted anhydride content	
PP-g-MA 002	37.2 (0.8)	8.1 (0.6)	37.5 (1.9)	43.8 (1.9)	40
PP-g-MA 003	20.4 (1.4)	4.8 (0.3)	17.4 (1.3)	22.3 (1.1)	20
PP-g-MA 004	11.4 (0.5)	2.3 (0.2)	8.7 (1.4)	11.0 (1.5)	10–12

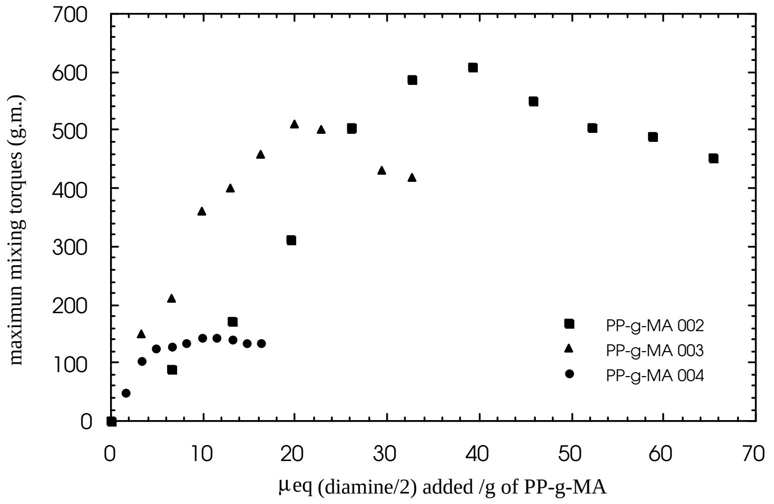

Fig. 13. Viscosimetric titration of the PP-g-MA 002, PP-g-MA 003 and PP-g-MA 004.

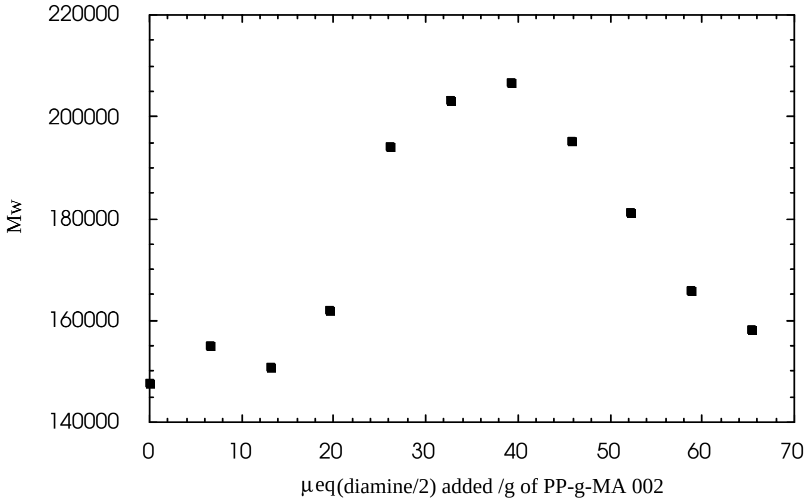

Fig. 14. Molecular weight (M_w) of the PP-g-MA 003 versus the half diamine concentration added.

all diamine concentrations, 11 mixings into the Brabender plastograph with 11 different concentrations have been carried out for each polymer. The maximum value of the torque for each PP-g-MA versus the half-diamine concentration added (imidised maleic anhydride concentration) are shown in Fig. 13 for PP-g-MA 002, 003 and 004. The maximum of these curves indicates the total maleic anhydride concentration of the studied PP-g-MA, i.e. 40, 20 and 10–12 µeq/g, respectively.

This quantification method assumes that the anhydrides are grafted onto the chain-ends and therefore give rise only to chain extension through the diamine reaction. This hypothesis is related to the mechanism we claimed for the PP grafting [1]. The study of the PP-g-MA 002 molecular weight (M_w) versus the half-diamine concentration added, presented in Fig. 14, does not contradict it: the concentration value at which M_w is maximum is comparable to the one at

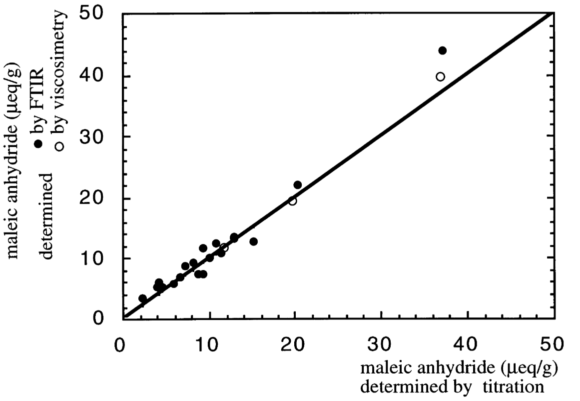

Fig. 15. Comparison of the maleic anhydride content measured out by titrimetric, viscosimetric and FTIR methods for various PP-g-MA.

which the torque is maximum (Fig. 13). Moreover no insoluble fractions were observed in the SEC solution, indicating the absence of gel in the product.

The acid–base titrimetric results are in good agreement with those obtained from viscosimetric titrations and spectroscopic measurements as summarised in Table 2.

A comparison carried out on higher grafted polypropylenes (study performed on PP-g-MAs synthesised in the laboratory or on those coming from various manufacturers [10]) are shown in Fig. 15. A good agreement between the results are obtained by the three methods.

The anhydride groups grafted onto polyethylenes or ethylene–propylene copolymers were titrated with success by the same method.

4. Conclusion

A large number of polypropylenes grafted with maleic anhydride can be accurately titrated with methanolic solutions of TBAOH as the titrating agent when a bromothymol blue coloured indicator is chosen despite drastic conditions needed by the polyolefins solutions (aprotic solvent and high temperature).

The studies of well-defined amounts of some anhydride compounds by titration, and the FTIR analyses of their reaction products after titration confirms that the TBAOH reacts always towards anhydride functions following a one-to-one stoichiometry whatever its form (open or closed).

These acid–base titration results are validated by FTIR spectroscopy quantification and by viscosimetric titration.

Moreover, this titrimetric method can be easily extended to the quantification of maleic anhydride grafted onto polyethylene and ethylene–propylene.

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